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RESEARCH ARTICLE

USING WIRE BEAM ELECTRODE (WBE) TO EVALUATE THE CORROSION BEHAVIOR OF ND STEEL IN ACID MEDIUM

Bo Zhao[a*],Yuxin Yu[a],Jing Guo[a], Tianyu Zhou[a], Shiwen Zou[b], Tong Xu[a]

[a] Materials Research and Evaluation Center, China Special Equipment Inspection and Research Institute, Beijing, 100013, China.
[b] Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, China.
**Corresponding Author E-mails: azhaobo19840626@163.com*

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ABSTRACT

In this article, wire beam electrode (WBE) was used to evaluate the corrosion behavior of ND steel in environmental acid atmosphere with different partial pressure of CO_2. Meanwhile, corrosion products and surface morphology analysis also used to support this research. The results showed that the corrosion behavior began from the edge of droplet in dew point corrosion, and gradually spread to the center of it. The spread speed would be increasing with CO_2 partial pressure enhance, which was 24h in 5% CO_2 and 4h in 50% CO_2. Corrosion current density in the edge of droplet can form the "cathode-anode-cathode ring" structure and disappears gradually as the corrosion time was going. Corrosion morphology observation results showed three ring shapes region and different elemental composition of different corrosion products, which is correspondence with the "cathode-anode We-cathode ring" structure measured in WBE experiments. The results showed that the reaction gradually transferred to the uniform corrosion on electrode surface when the dew point corrosion reaction reaching the late stage. It comes from the dissolution, diffusion and reaction of gaseous corrosion medium of CO_2 and O_2.

KEYWORDS

wire beam electrode, CO_2, Corrosion.

1. INTRODUCTION

Dew point corrosion (DPC) is the most important type of high temperature equipment corrosion (Dan et al., 2011; Wang et al., 2013). Some researchers' consideration that DPC is a kind of special corrosion in thin electrolyte film, and the corrosion rate was due to the rate of corrosion media mass-transfer process. As for DPC, the corrosion media is different to the common thin electrolyte film, the acid atmosphere such as SO2, SO3, CO2 and HCl are became the corrosion media instead O2 to attack the base metal (Shu et l., 1999; Huijbregts and Leferink, 2004).

2. EXPERIMENTAL

2.1 Materials preparation

The metal we chose is 09CrCuSb steel (ND steel), which is a new type of low alloy steel used in DPC environment. The chemical compositions showed Table 1, referring to standard of GB/T150.2-2015. As the result showed, the chemical compositions of this steel are kept according to the requirements of the standards, and it used to make the electrodes and observation samples.

Table 1: The chemical compositions of ND steel.

Ele.	C	Si	Mn	P	S	Cr	Cu	Sb
Std.	≤0.12	0.20~0.40	0.35~0.65	≤0.030	≤0.020	0.70~1.10	0.25~0.45	0.04~0.10
Samp.	0.10	0.16	0.42	0.010	0.008	1.05	0.33	0.08

Figure 1 is the metallographic structure of ND steel. As the results, its microstructure is ferrite with a few pearlite and carbides.

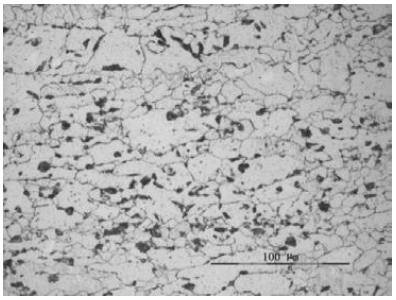

Figure 1: The metallographic structure of ND steel.

2.2 Wire beam electrode measurement

In order to study the transfer mass-transfer characteristics, wire beam electrode (WBE) measurement were used to evaluate the surface current distribution on the ND electrode. The WBE is formed with an11×11 wire bundle electrode arrays (121 electrodes). Every electrode cuts into a cylinder with 1mm surface diameter and sealed into an epoxy resin cube with 0.3mm interval. The working surface of the WBE was subsequently ground with 150 to 2000 grit emery papers, and then cleans it with distilled water and acetone after polishing. The measurement was

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performed with a Corttest CT520 WBE scan workstation with the surface current scanning model, and the result presents current distribution on surface.

We used a work-holding device to hold the WBE work surface keep up, and dropped 0.5ml distilled water on it formed a single corrosive droplet. In order to prevent the droplet evaporation, WBE set in a constant temperature and constant humidity chamber with 25℃and 100%RH. The internal dimensions of the chamber (*l*×*w*×*h*) is 100×100×50mm, and inject 5%and 50% CO_2 acid gas mixed by CO_2 and N_2 with flow rate of 100ml/min, making the saturated acid atmosphere. In this experiment, 121 electrodes which coupled together are disconnected successively, and the couples current between each electrode and the other electrodes were measured respectively. Scanning time are 0, 2, 4, 8, 24, 48 hours after corrosion occurrence, totally 6 times.

3. Results and Discussion

3.1 Results of wire beam electrode measurement

Figure 2 showed the change of current distribution on ND steel surface in5% CO_2 acid atmosphere. In this experiment, all surface of WBE cell was covered by distilled water droplets, and the abscissa and ordinate coordinates represent different electrode positions. It can be seen that the positions located on the edge and the center of WBE surface showed the lowest distribution current value at 0 h, and it presents those positions became cathodes in this reaction. At the same time, the distribution current close to the edge showed the highest distribution current value, and became anode. The corrosion current formed a structure of "cathode-anode-cathode ring" from the outer edge to the center under droplets, and the position of anode might be the area that corrosion reaction is the most serious. Therefore, the corrosion current reached 0.0265μAat 0h in anode area.

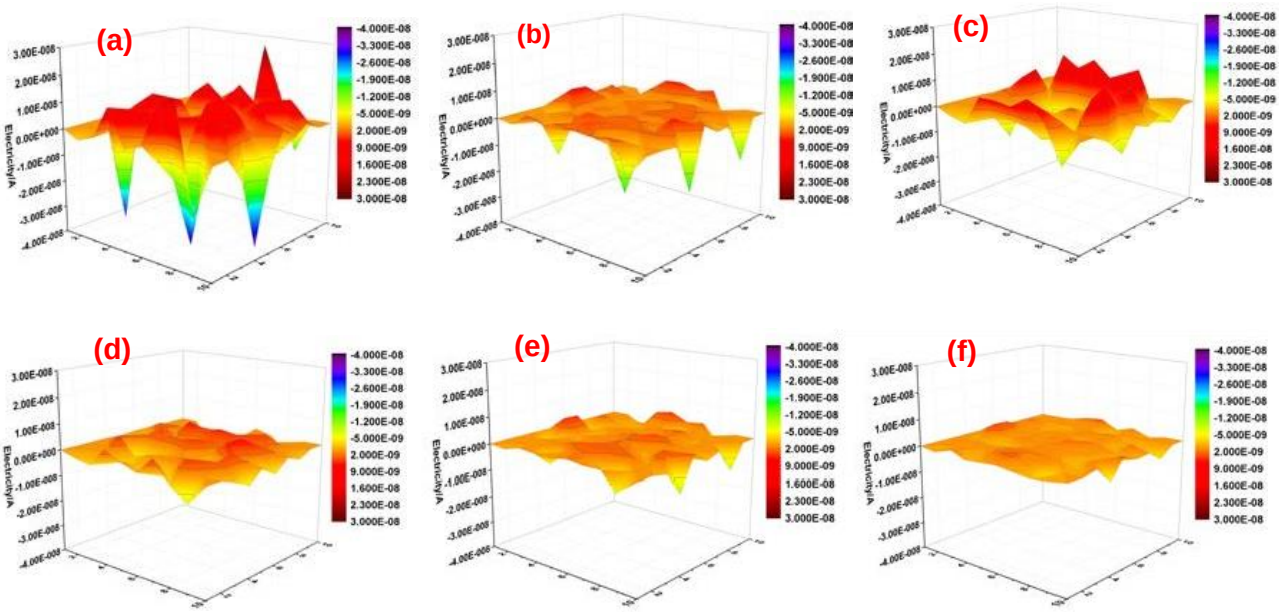

Figure 2: The change of current distribution on ND steel surface in5% CO2 acid atmosphere (a)0h, (b)2h, (c)4h, (d)8h, (e)24h, (a)48h.

Cathode current at the edge of WBE disappeared gradually as the corrosion time was going, and the position of the anode was not changed basically, but the current value decreases gradually. The maximum anodic current values reached 0.0157, 0.0066 and 0.0059μA at time after corrosion time of 2h, 4h, 8h respectively, which were 41%, 75% and 76% lower than 0h.The corrosion reaction tended to stable at 8h, and the electrode surface could not observe the characteristics of separation of anode and cathode. The corrosion proceeded more smoothly on the surface of the electrode, and the corrosion characteristics were mainly uniform corrosion.

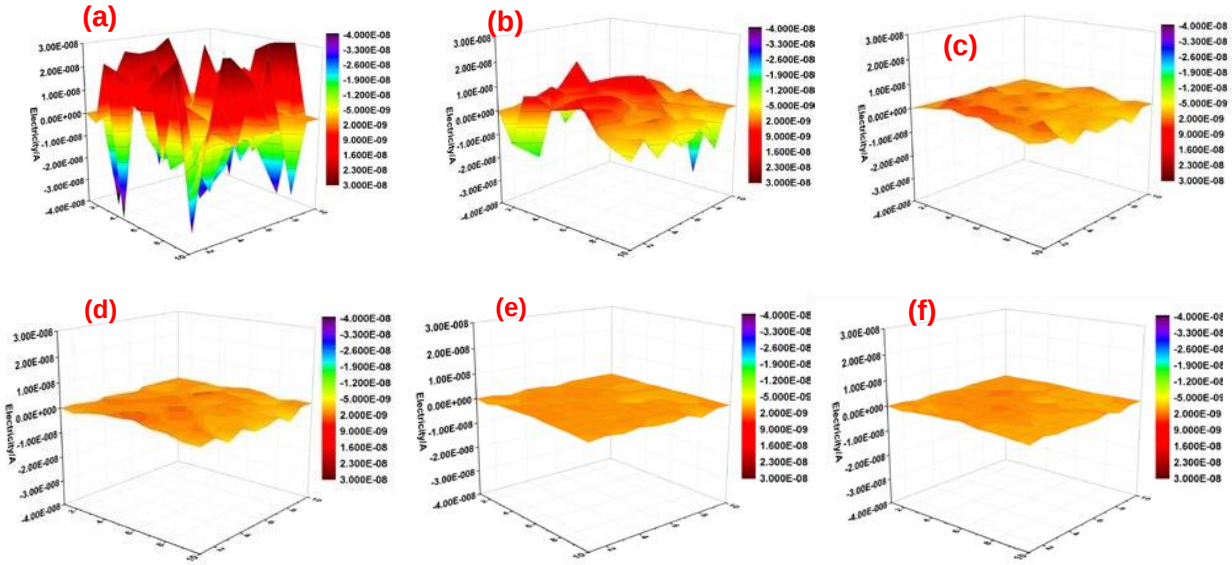

Figure 3: The change of current distribution on ND steel surface in50% CO2 acid atmosphere (a)0h, (b)2h, (c)4h, (d)8h, (e)24h, (a)48h.

Figure 3 showed the change of current distribution on ND steel surface in5% CO_2 acid atmosphere. As the results, the distribution of cathode and anode on WBE surface in 50% CO_2 environment is similar to that in 5% CO_2 environment at the initial stage of corrosion reaction, but it is much more severe. The maximum anodic current reached about 0.0328μA at 0 h, which is about 1.24 times higher than that in 5% CO_2 environment. The current density of the anode decreases gradually as the corrosion time was going, and it is faster than that in 5% CO_2 environment. The separation of anode and cathode has been slight in electrochemical reaction at 4h, and then stabilized at 24h.That means that the corrosion degree on the WBE surface has declined, and it tended to the uniform corrosion. Figure 4 showed the comparison of the maximum current on WBE surface with 5% and 50% CO_2. It can be seen that the maximum surface current of ND steel has similar change tendency in the two different concentration of CO_2content environment. All of them have the highest surface current at 0 h, which decreases rapidly as the corrosion time was going. 5% CO_2 reached steady state at 8h, while0% CO_2 reached steady state at 24h.

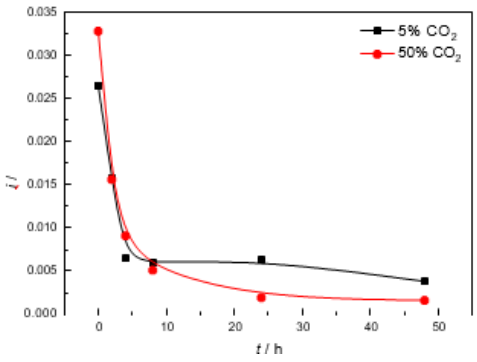

Figure 4: Comparison of the maximum current on WBE surface with5% and 50% CO_2.

The experiment results in 5% and 50% CO_2atmosphere all point to that the reaction gradually transferred to the uniform corrosion in all beam on the surface of every single electrodes as the corrosion time was going, and the characteristics of the galvanic reaction of the electrode decreased gradually.

4. Discussion

According to previous research, the corrosion reaction will be greatly different with different shape under thin electrolyte film. As for this research, the work electrode is ND steel, and the anodic reaction is Fe dissolution. The chemical equations is shown as follows (Wilson, 1923; Martinez and Stern, 2001):

Anodic:

$$Fe \rightarrow Fe^{2+} + 2e \quad (1)$$

In the reaction process, the origin solution is distilled water with high resistivity, which can form the acidic solution while the vapor phase CO_2 dissolves in it. And then the solute can be ionized, with a part of depolarization ions change. The chemical equations are shown as follows:

Dissolution and Ionization of CO_2:

$$CO + H\,O \leftrightarrow H\,CO_3 \quad (2)$$

$$H\,CO \leftrightarrow H^+ + HCO + e \quad (3)$$

$$HCO^- \leftrightarrow H^+ + CO + 2e \quad (4)$$

According to the equations, the ionization of CO_2 dissolved in water can be divided to two steps. The primary ionization constant Ka(H_2CO_3) is 4.3×10^{-7} and the secondary ionization constant Ka(HCO_3^-) is 5.61×10^{-11}in the room temperature of 20°C.Considering that saturated solubility of CO_2 is 0.04 mol/L in this situation, the theoretical maximum pH of this solution is pH=3.94.Therefore, both two types cathodic reaction of the electrodes of hydrogen evolution and oxygen absorption may exist at the same time. So that, the cathodic reactions are much more complex relatively, and the chemical equations is shown as follows:

Cathodic reactions:

$$O + 4H\,O + 4e^- \rightarrow 4OH^- \quad (5)$$

$$2H^+ + 2e^- \rightarrow H \quad (6)$$

According to the anodic and cathodic reactions, the corrosion process is shown in Fig.5. For the N_2 and CO_2 and moisture atmosphere continuous injection, it corresponds to a variety of atmospheric environments with N_2, CO_2 and O_2 in the experimental environment.N_2 and O_2 dissolve intoH_2O is process, while CO_2 dissolution is both physical and chemical process. So that, CO_2 reaching the solution interior is much more easily than O_2.

In the reaction process, the edge of droplet is the thinnest area, and forms a thin electrolyte film because of its shape. It is more easily that oxygen permeates into the droplet and reaches the surface of the substrate. So the edge of droplet is oxygen-rich and presents cathode characteristic (Shu et al., 2000). The area beside the edge of droplet has low oxygen content and high CO_2 content, so it presents anode characteristic. At the same time, the center of electrode has a relatively thick electrolyte film, and solution is origin without CO_2 and its reaction. So that it also presents cathode characteristic, explaining why it can form the structure of "cathode-anode-cathode ring".

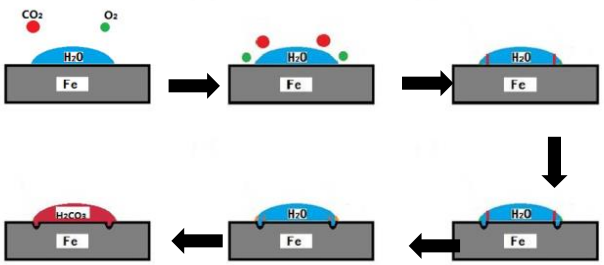

Figure 5: The mechanism of dew point corrosion of ND steel in acid atmosphere.

CO_2 dissolved gradual increase as corrosion reaction going, and concentration diffusion dominates the corrosion reaction process. H_2CO_3 diffuse into droplet interior, and H^+ will become the dominant anion in depolarization reaction. Corrosion scale of $FeCO_3$blocks on the electrode surface of in large quantities as corrosion reaction going, and hinders the mass transfer process of O_2 further. Therefore, the corrosion on the surface of the electrode becomes independent reaction in the later stage, and the difference between the cathode and anode regions is not obvious.

5. Conclusion

The dew point corrosion reaction under a droplet in acid atmosphere can form the "cathode-anode- cathode ring" structure from the outer edge to the center under droplets, and the anode region corrosive more serious. Cathode current at the edge of WBE disappear gradually as the corrosion time was going, but the time of reaching stationary current density on electrode surface in 50% CO_2 is more rapid than it in 5% CO_2 atmosphere. The results point to that the reaction gradually transferred to the uniform corrosion on electrode surface when the dew point corrosion reaction reaching the late stage, and the characteristics of the galvanic reaction of the electrode decreased gradually. It comes from the dissolution, diffusion and reaction of gaseous corrosion medium of CO_2 and O_2.

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